



The dynamic-state effects of sodium ion contamination on the solid polymer electrolyte water electrolysis



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HIGHLIGHTS

- The dynamic-state effect of Na⁺ on the SPE water electrolysis is studied.
- Operation conditions significantly affect the degradation.
- Anode poisoning causes more severe degradation than cathode poisoning.
- The degradation is mainly attributes to the increase in cathode overpotential.
- The reaction $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ takes place at cathode.

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ABSTRACT

Na⁺ is a likely intrinsic impurity in water and is a potential cation impurity in the solid polymer electrolyte water electrolysis. In this paper, the dynamic-state effect of low concentration of Na⁺ is studied by adding Na⁺ into the deionized water fed in the SPE water electrolyser. The dynamic variation of cell voltage results show that the cell performance degraded more severely in the presence of Na⁺ impurity by anode poisoning than by cathode poisoning. The severity and poisoning rate of the cell depend on the Na⁺ concentration, water flow rate and cell temperature. However, the current density does not impact the extent of the cell voltage increase. In the meantime, an external reference electrode is used to measure the anode and cathode potentials. The performance degradation is mainly ascribed to the increase in cathode overpotential by anode poisoning. EIS measurements show that the performance difference primarily comes from the kinetics loss rather than the ohmic loss. The decrease of available protons in the three phase boundaries may lead to the increase in charge transfer resistance. The electron probe microanalysis tests show that Na⁺ remains in CCM even recovered with deionized water, which results in only partially recovered cell performance.

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1. Introduction

Hydrogen is an efficient and clean energy source and will be widely used in the future [1]. The solid polymer electrolyte (SPE) water electrolysis is considered to be a very promising technology of producing hydrogen from renewable energy source [2,3]. And it possesses significant advantages compared with the conventional alkaline electrolyte water electrolysis, including greater operating safety, higher product purity and energy efficiency [4–9].

During water electrolysis operation, cationic contaminations originating from stack component materials and feed water can

cause serious performance degradation of electrolyser. The impurities will produce a progressive increase of cell voltage or a decrease of current density [6,10], because these cations have higher affinity than protons for the sulfonic acid group sites and replace protons in accord with normal ion exchange processes in the ionomer phase [11–14]. The cationic impurity could significantly reduce the conductivity of the membrane and reduce water content in the fully hydrated membranes by replacement of protons [11,15]. Furthermore, platinum is the best electrocatalyst for hydrogen evolution in acid media and it is extremely sensitive to poisoning by under potential deposition (UPD) of monolayer of other metals. NiSO₄ in the feed water resulted in a strong decrease in current density because the platinum surface was covered by nickel deposition and proton discharge took place on nickel with a

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much higher cathodic overvoltage than on bare platinum [4]. It was found that the UPD of Cu monolayer produced an overpotential increase of 160 mV at 100 mA cm^{-2} during hydrogen evolution for platinum electrode [10]. Moreover, Kotz and Stucki [16] demonstrated that the poisoning of platinum in the presence of Cd^{2+} or Cu^{2+} ions occurred immediately, causing steep overpotential increase during hydrogen evolution in acid media.

Sodium ion is a common impurity in the feed water. It has very negative Nernst potential and cannot be reduced at the cathode. Only a few researches about the influence of Na^+ on fuel cells were reported. The in situ contamination results showed that Na^+ impurities could exchange with protons in the cathode catalyst layer, which resulted in the dramatic decrease of the fuel cell voltage mainly due to the cathode overpotential increase [13]. In addition, Na^+ in the air stream at the cathode side severely affected the performance of a proton exchange membrane fuel cell, which is primarily caused by ohmic losses due to the displacement of protons by Na^+ [17,18]. In the aspect of modeling, the simulation showed that the cationic contaminants will always be more concentrated on the cathode side, and decrease the exchange current density and the limiting current by decreasing the available protons in the cathode catalyst layer [19]. In our previous work, the influence of high concentration of Na^+ (0.05 mol L^{-1}) on the SPE water electrolysis was studied [20]. Based on previous study results, high concentration of Na^+ causes serious performance degradation to SPE water electrolyser, which mainly resulted from the cathodic overpotential increase. Additionally, it was found that the pH of cathode outlet water increased to above 11.0 due to the reaction of $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. From a practical point of view, the concentration of contaminant is extremely low in the feed water. Accordingly, it is important to study the influence of low concentration of Na^+ for the application of SPE water electrolysis.

In this work, the dynamic-state effect of low concentration of Na^+ on the SPE water electrolysis was investigated. The influence of different operating conditions were also investigated, including Na^+ concentrations, feed water flow rates, cell temperatures and current densities.

2. Experimental

2.1. Materials and fabrication

Ir black (HiSPEC 16000, Johnson Matthey) and Pt/C catalyst (70 wt.%, HiSPEC 13100, Johnson Matthey) were used as anode and cathode electrocatalysts, respectively. To prepare the catalyst coated membrane (CCM), a homogeneous ink consisting of catalyst, Nafion solution (5 wt.%, DuPont) and isopropanol was sprayed onto each side of a Nafion 115 membrane. The resulting loading of Ir black and Pt/C was 2 mg cm^{-2} and 1 mg cm^{-2} , respectively. The Nafion content was 25 wt.% for both sides. The platinum-plated porous titanium plate and carbon paper (Toray H-060) were used as anode and cathode current collector, respectively. The membrane electrode assembly (MEA) was fabricated by hot pressing the CCM and carbon paper together at 140°C under a pressure of 1 MPa for 2 min. The effective area of the MEA was about 5 cm^2 .

2.2. Single cell tests and electrode potential measurements

The single cell tests were carried out with a SPE water electrolyser (Fig. 1a). The end plate was made of stainless steel. The porous titanium plate and stainless steel mesh were used as anode current collector and cathode flow field, respectively.

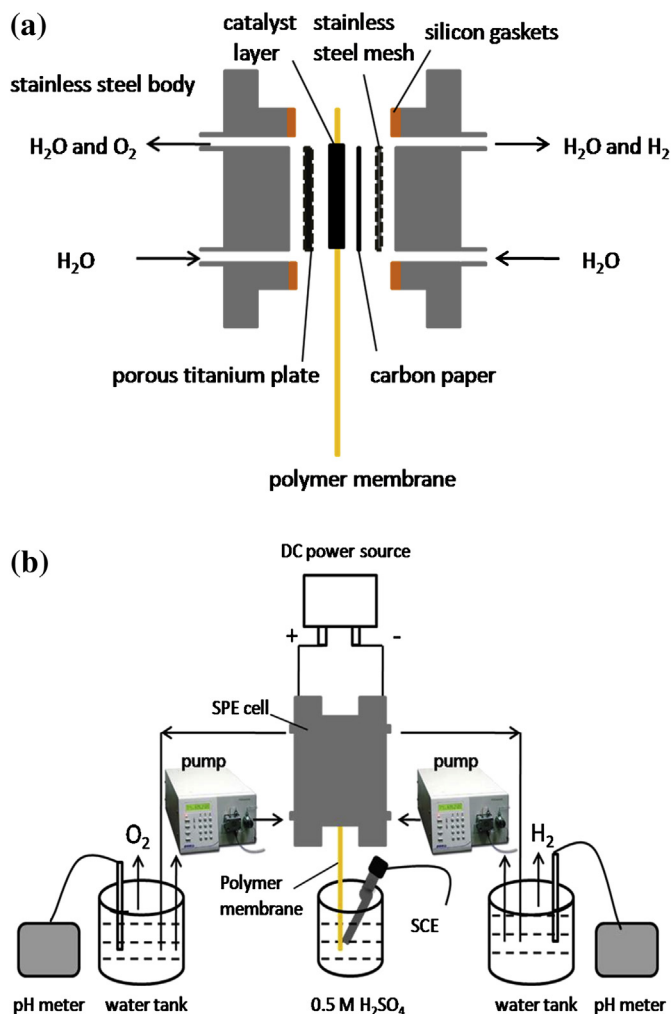


Fig. 1. (a) Sketch of the single SPE cell; (b) Sketch of the single cell test stand of water electrolysis.

The cell was operated galvanostatically at 500 mA cm^{-2} and the cell temperature was kept at 60°C with deionized water feeding to anode and cathode. In the anode poisoning, the contaminant was fed to the anode with deionized water containing Na_2SO_4 , and the concentration of Na^+ impurity was varied as 0.001, 0.002, 0.005 mol L^{-1} . Similarly, the cathode poisoning study was followed by the same procedure. The pH values of the anode and cathode outlet water were monitored by basic pH meter PB-10 (Sartorius AG) during the whole experiment.

To investigate the dynamic-state effect of Na^+ and the poisoning mechanism, the anode and cathode electrode potentials should be measured separately. An external reference electrode was introduced, as mentioned in Refs. [13,14,21]. The anode and cathode electrode potentials were measured against a saturation calomel electrode (SCE, $E = 0.242 \text{ V vs. RHE}$). As shown in Fig. 1, the extending part of Nafion membrane in the MEA was immersed in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution. The end of the reference electrode (SCE) was positioned close to the Nafion sheet to reduce solution ohmic potential drops. Using this method, the ionic contact was assured through forming a bridge between the MEA and H_2SO_4 solution [13]. The anode and cathode potential was measured separately by a multimeter, from which one of the leads was connected to the anode or cathode and the other was connected to the reference electrode. The electrode potentials

were first measured against SCE and finally calibrated against RHE.

2.3. Electrochemical and physical characterizations

Electrochemical impedance spectroscopy (EIS) of the SPE water electrolysis cell was performed at 1.45 V vs. RHE by using a PARSTAT 2273 (EG& G instruments) [22]. The anode served as the working electrode, while the cathode served as the counter electrode and reference electrode at the same time. The measurement was conducted over frequencies ranging from 100 kHz to 0.1 Hz with a sinusoidal potential perturbation of 10 mV. The EIS data were modeled with ZsimpWin software.

The elemental distribution on the cross-section of the polluted and recovered CCMs was analyzed by a SHIMADZU EPMA-1600 electron probe microanalyzer (EPMA).

3. Results and discussion

3.1. Effect of Na^+ in anode poisoning

The dynamic-state effect of $0.001 \text{ mol L}^{-1} \text{ Na}^+$ with 1 ml min^{-1} on the SPE water electrolysis cell performance in anode poisoning is shown in Fig. 2(a). The cell was operated galvanostatically at 500 mA cm^{-2} with deionized water feeding to the anode for 1 h,

and then $0.001 \text{ mol L}^{-1} \text{ Na}^+$ pollutant was fed to the anode. The performance of the cell degenerated dramatically and the cell voltage firstly increased to 1.84 V in about 3 h and then increased sharply to 2.20 V in about 2 h. Finally, the cell voltage increased slowly to 2.24 V in about 4 h.

To understand the reason for the increase in cell voltage, an external reference electrode was developed to separate the anode and cathode overpotential from each other [13,21]. The anode and cathode potentials were measured against SCE reference electrode and finally calibrated against RHE. And the cell voltage is the potential difference between anode and cathode. Therefore double axis standards were used in Fig. 2. Different from high concentration (0.05 mol L^{-1}) poisoning [20], the anode potential first increased and then decreased to a stable potential at low concentration of Na^+ . As shown in Fig. 2(a), the anode potential first increased from 1.64 V to 1.79 V in 3 h and then decreased to 1.68 V in 2 h. Meanwhile, the cathode potential decreased gently to -0.08 V in 3 h and then decreased sharply to -0.53 V in 2 h. After recovered with deionized water, the cathode potential recovered quickly from -0.60 V to -0.21 V in about 2 h, and then recovered slowly to -0.10 V in about 18 h. The dramatic variations of cell voltage are mainly ascribed to the change of the cathode overpotential, accordingly, it can be deduced that Na^+ poisoning can affect the cathode reaction.

In order to investigate the cause of the anode and cathode potential changes, the pH of the outlet water were monitored. As

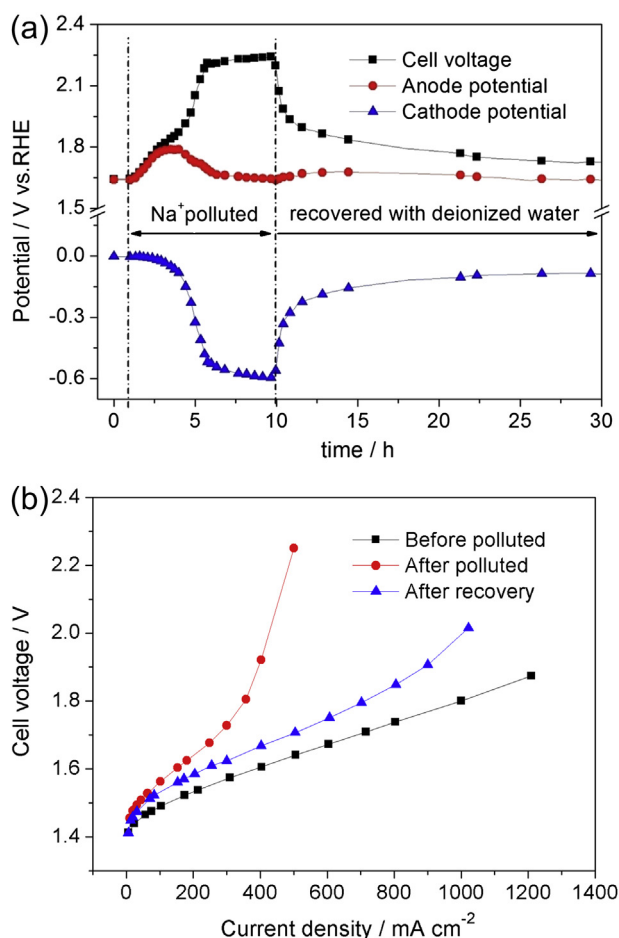


Fig. 2. (a) The effect of $0.001 \text{ mol L}^{-1} \text{ Na}^+$ on the cell performance by anode poisoning, and recovery with deionized water. At 60°C , 500 mA cm^{-2} with flow rate 1 ml min^{-1} . (b) Comparison of the polarization curves before polluting, after polluting and recovered with deionized water.

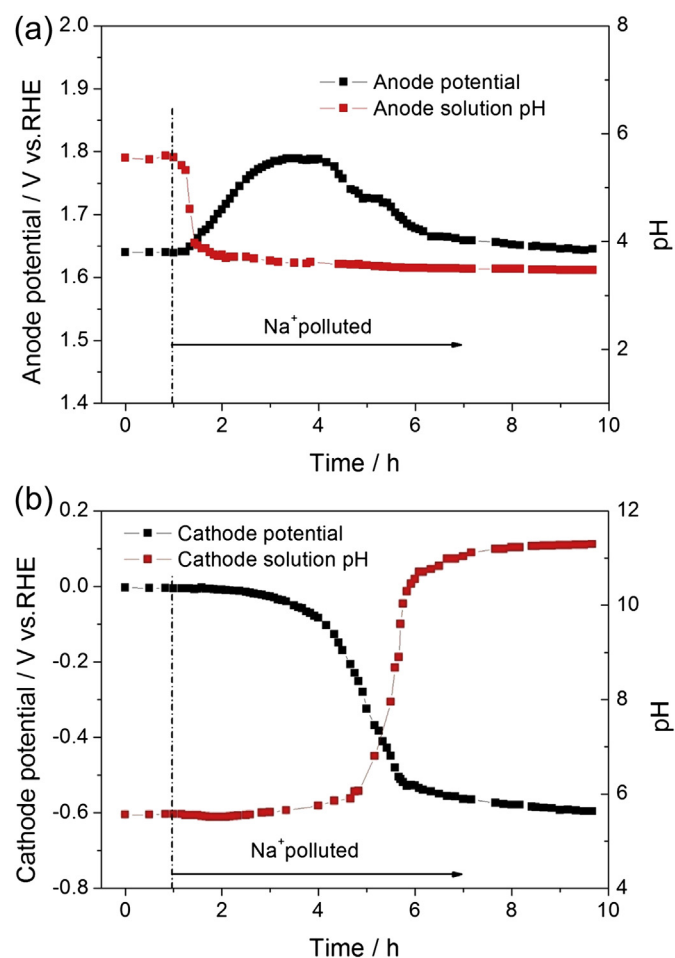
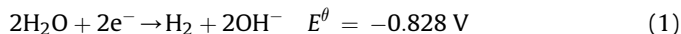


Fig. 3. (a) Anode potential vs. time and anode water pH vs. time; (b) cathode potential vs. time and cathode water pH vs. time for the cell poisoning by $0.001 \text{ mol L}^{-1} \text{ Na}^+$ at 60°C , 500 mA cm^{-2} with flow rate of 1 ml min^{-1} .

shown in Fig. 3(a), before poisoning, the anode and cathode outlet water pH were 5.6 because of the dissolution of CO_2 in the atmosphere [23]. After poisoning by Na^+ , the protons in the Nafion polymer electrolyte at the anode catalyst layer were exchanged with sodium ions [11,13,14] and then entered into the feed water. Accordingly, H_2SO_4 was included in the anode feed water, which decreased the anode outlet water pH from 5.6 to 3.8 immediately (Fig. 3(a)). Meanwhile, as shown in Fig. 3(b), the cathode potential decreased to -0.08 V and the pH of cathode outlet water increased slightly from 5.6 to 5.8 in about 3 h. Thereafter the pH of cathode outlet water increased dramatically to 11.3 with the cathode potential decreasing steeply to -0.60 V. The changes are presumably caused by the following reaction at the cathode:



The theoretical cathode potential is -0.65 V when pH is 11.3, and the measured cathode potential is about -0.60 V. The experimental results verified the conjecture. The cathode feed water became alkalic, because both the Na^+ transferred from the anode and OH^- produced at the cathode entered into the cathode feed water.

After pollution, sodium ions were driven from anode to cathode by concentration gradient and electric field. As a result, the distribution of Na^+ reached equilibrium between the MEA and feed water. The specific conductivity κ (S cm^{-1}) of membranes is a function of the membrane composition x_{H} and it can be expressed by the following equation [13]:

$$\kappa = FC_{\text{SO}_3}(u_{\text{H}}x_{\text{H}} + u_{\text{Na}}(1 - x_{\text{H}})) \quad (2)$$

where F is Faraday constant, C_{SO_3} is the concentration of the cation exchange site in the membrane, u_{H} and u_{Na} are the mobility of proton and Na^+ , respectively, and x_{H} is the cationic site fraction of H^+ . The mobility of Na^+ is lower than that of proton for its higher affinity for the sulfonic acid group sites in the polymer electrolyte [12,14]. The specific conductivity κ will decrease after the membrane is poisoned by Na^+ , thus the cell voltage will increase at constant current density. However, the migration velocity of Na^+ is slow under low cell voltage. And Na^+ contaminants accumulate in the anode catalyst layer and membrane. The water oxidation occurred at the anode catalyst layer is given as: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. Proton is the product in the anode catalyst layer. Thus the accumulation of Na^+ in the anode catalyst layer and membrane will hinder the water oxidation [13], and causes the increase of anode potential. With the increase of cell voltage, the migration velocity of Na^+ increases and the amount of Na^+ at the anode catalyst layer will decrease. Gradually, the distribution of Na^+ becomes uniform in the MEA and reaches equilibrium between MEA and feed water so that the anode potential decreases and then becomes stable. With migrating of Na^+ from the anode to cathode, the protons in membrane and Nafion polymer electrolyte at the cathode are partially replaced by Na^+ . The cathode potential decreases slowly for the decline in concentration of protons. Since protons were replaced by sodium ions, there will be not enough protons for cathodic reduction reaction. At constant current density, the lack of protons at cathode will cause the reaction (1) to take place, which results in rapid decline in cathode potential and steep increase in pH value of cathode feed water.

Fig. 2(a) also shows that the cell performance can be partially recovered when deionized water was fed to the anode. The cell voltage decreased quickly from 2.24 V to 1.90 V in 2 h, and then recovered slowly to 1.72 V in 18 h. The polarization curves in Fig. 2(b) also show that the cell performance is partially recovered with deionized water.

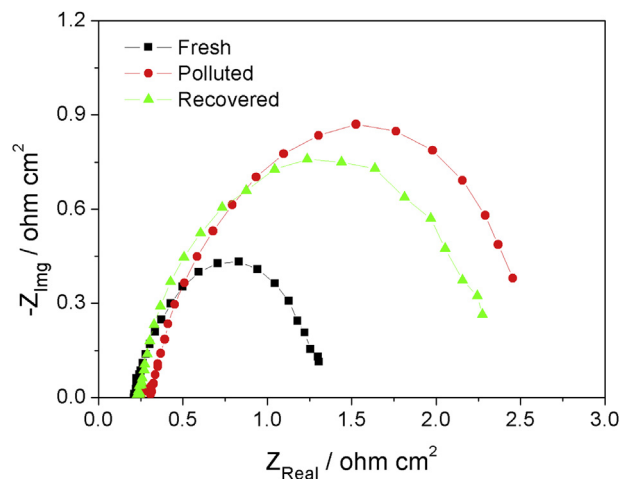


Fig. 4. Nyquist plots for the SPE cells before and after polluting by anode poisoning and cell after recovery with deionized water.

To get more insights into the effect of Na^+ , the electrochemical impedance of the cell was carried out at 1.45 V. A comparison of Nyquist plots is presented in Fig. 4. It can be seen that only one semicircular loop can be observed in the Nyquist plot. The high frequency intercept on the real axis R_Ω of the fresh cell, which represents the total ohmic resistance of the single cell [24], is smaller than that of the polluted cell and recovered cell. Moreover, the arc diameter of the fresh cell, which is a measure of charge transfer resistance R_{ct} [24], is also smaller than that of the polluted cell and recovered cell. R_Ω and R_{ct} can be calculated through simulation with $L R_\Omega (R_1 Q_1) (R_{\text{ct}} Q_{\text{dl}})$ equivalent circuit [22], and the calculation results are shown in Table 1. Both R_Ω and R_{ct} increase after Na^+ poisoning. After recovery, R_Ω and R_{ct} are decreased but still larger than that of the fresh cell. The occupation of ion exchange sites by Na^+ in the catalyst layers and membrane causes the increase in ionic resistance. However, the changes of ohmic overpotential are less than 50 mV. Consequently, the performance degradation primarily comes from the kinetics loss rather than the ohmic loss. Based on the agglomerate model, the microstructure of the porous catalyst layer can be depicted as catalyst particles covered with electrolyte [25,26]. In the catalyst layer, the interface of the reactant or product contacts with catalyst particles and Nafion polymer electrolyte is the three phase boundaries (TPB) where the redox reaction takes place. The catalyst provides catalytic sites and Nafion polymer electrolyte provides delivery channel of protons. Considering the agglomerate model, it was supposed that the cathode reaction should be under the control of protons transport in the Nafion polymer electrolyte [27]. A lack of available protons in the TPB of catalyst layers after Na^+ poisoning will not only increase ohmic resistance but also hinder protons leave or transfer to the catalytic sites, which leads to the increase in charge transfer resistance R_{ct} and the decrease in exchange current density [13,19]. This will lower the reaction rate and increase the overpotential at a given current density. After recovery, more protons are available in the TPB of catalyst layers. That is the very reason for the partially recovered cell performance.

Table 1

Ohm resistance of the cell polluted by anode poisoning with $0.001 \text{ mol L}^{-1} \text{ Na}^+$ and recovered with deionized water.

Sample	Fresh	Polluted	Recovered
R_Ω ($\Omega \text{ cm}^2$)	0.21	0.31	0.23
R_{ct} ($\Omega \text{ cm}^2$)	1.12	2.40	2.10

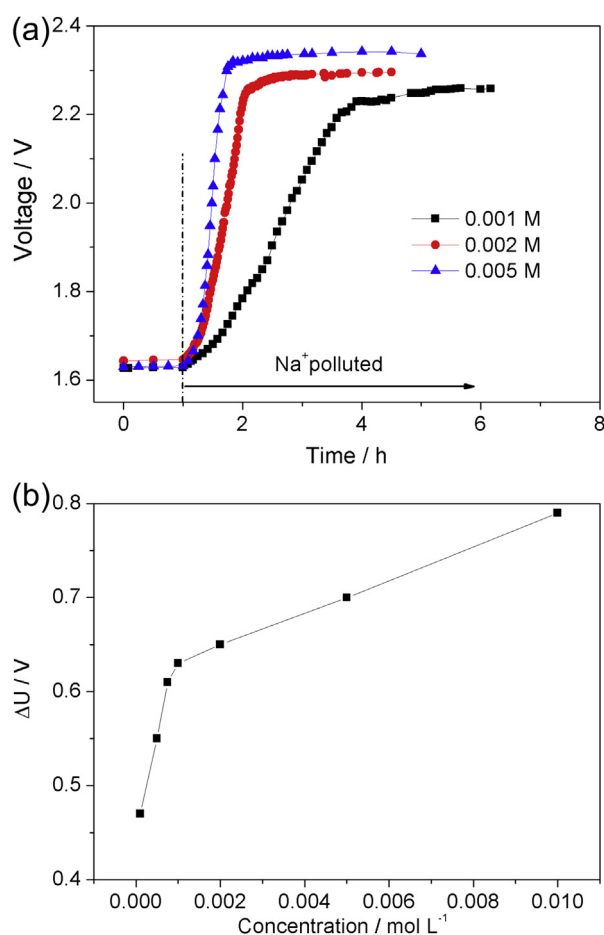


Fig. 5. (a) The effect of Na⁺ concentration on the cell performance by anode poisoning with flow rate of 5 ml min⁻¹; (b) The relationship between the concentration of Na⁺ and the cell voltage increase.

Fig. 5(a) shows the cell voltage, measured at 500 mA cm⁻², as a function of time during poisoning with different Na⁺ concentrations. It is clear that the poisoning rate and the voltage increase are a strong function of the Na⁺ concentration. With higher concentration, the faster poisoning rate and the greater voltage increase are observed. During poisoning by 0.001, 0.002 and 0.005 mol L⁻¹ Na⁺, it took about 3, 1 and 0.6 h for the cell voltage to be stabilized and the voltage increase were about 0.63, 0.65 and 0.71 V, respectively. The relationship between Na⁺ concentrations and voltage increase in Fig. 5(b) can be expressed by the following formulas. 0.0001 mol L⁻¹ of Na⁺, which is several ppm, even cause 0.468 V cell voltage increase. It indicates that the SPE water electrolysis is very sensitive to Na⁺ impurity for Na⁺ is prone to accumulating in the Nafion polymer electrolyte of catalyst layers and Nafion membrane for higher affinity of Na⁺ than protons for the sulfonic acid group sites [11–14]. Even at very low concentration, Na⁺ impurity can hinder the transport of protons in the catalyst layers and induce severe deterioration in electrolysis performance.

$$\Delta U = 0.613 + 17.6 C \quad (0.001 \text{ mol L}^{-1} \leq C \leq 0.01 \text{ mol L}^{-1}) \quad (3)$$

$$\Delta U = 0.447 + 214 C \quad (0.0001 \text{ mol L}^{-1} \leq C < 0.001 \text{ mol L}^{-1}) \quad (4)$$

ΔU is the increase of cell voltage, and C is the concentration of Na⁺ in the anode feed water.

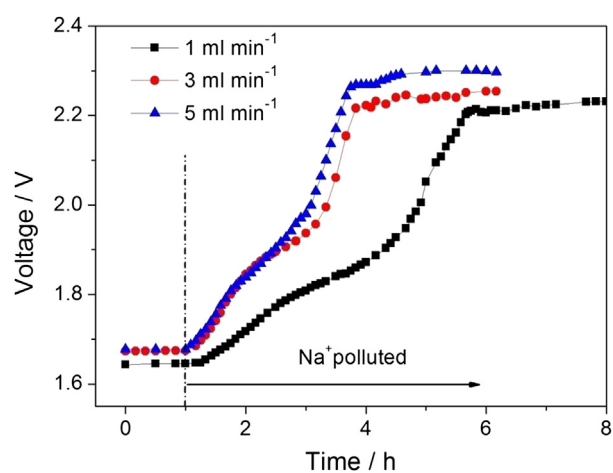


Fig. 6. The effect of flow rates on the cell performance at 500 mA cm⁻², T_{cell} = 60 °C, 0.001 mol L⁻¹ Na⁺ solution.

Fig. 6 shows the effect of the flow rate on the cell performance at 0.001 mol L⁻¹ Na⁺ poisoning. Similar to the effect of the sodium ion concentration, the faster poisoning rate and greater voltage increase are observed at higher flow rate. With faster flow rate, there are more sodium ions entering into the cell in a settled time, which causes higher voltage increase.

The effect of cell temperature on the cell performance is shown in Fig. 7. The poisoning rate increased with decreasing temperature, and the voltage increased by 0.16 V (60 °C), 0.25 (45 °C) and 0.27 V (30 °C) after poisoning for 1 h. With the decrease of temperature, the mobility of Na⁺ declines. It will take longer time for Na⁺ to get equilibrium in the MEA and cause larger voltage increase. The final voltage increases were about 0.63 V (60 °C), 0.64 V (45 °C) and 0.67 V (30 °C), respectively, when the cell reached a steady state.

Fig. 8 shows the effect of the current density on the cell performance during the anode poisoning by 0.001 mol L⁻¹ Na⁺. Similar to the effect of the Na⁺ concentration, the poisoning rate showed a close relationship with the current density. After poisoning for 1 h, the voltage increased by 0.16 V at 500 mA cm⁻² in comparison with 0.27 V at 750 mA cm⁻² and 0.37 V at 1000 mA cm⁻². Although the poisoning rates are different, the extent of poisoning was the same, that is, the voltage increases are about 0.63 V after poisoned for 5 h at different current densities, indicating that the MEAs have the identical equilibrium concentrations of Na⁺ after poisoning by the same concentrations of Na⁺.

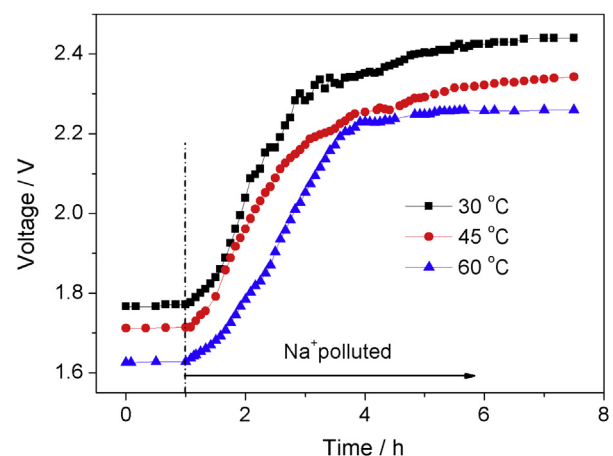


Fig. 7. The effect of temperatures on the cell performance at 500 mA cm⁻² with 5 ml min⁻¹ Na⁺ solution at the anode.

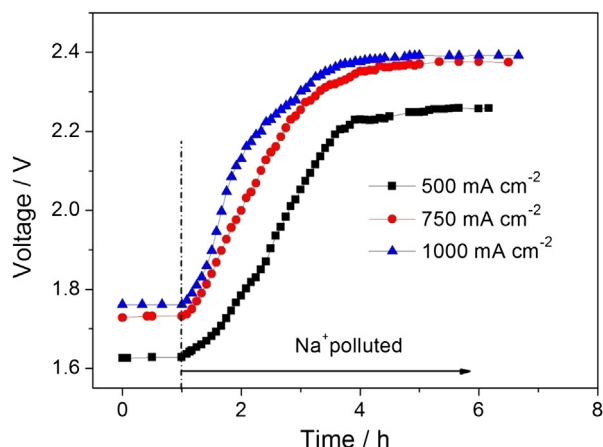


Fig. 8. The effect of current densities on the cell performance. $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$ with $5\text{ ml min}^{-1}\text{ Na}^+$ solution at the anode.

3.2. Effect of Na^+ in cathode poisoning

The effect of $0.001\text{ mol L}^{-1}\text{ Na}^+$ on the cell performance in cathode poisoning is shown in Fig. 9(a). The voltage and anode potential increased to 1.70 V and 1.67 V in about 1 h and then increased slowly to 1.73 V and 1.69 V in about 6 h, respectively.

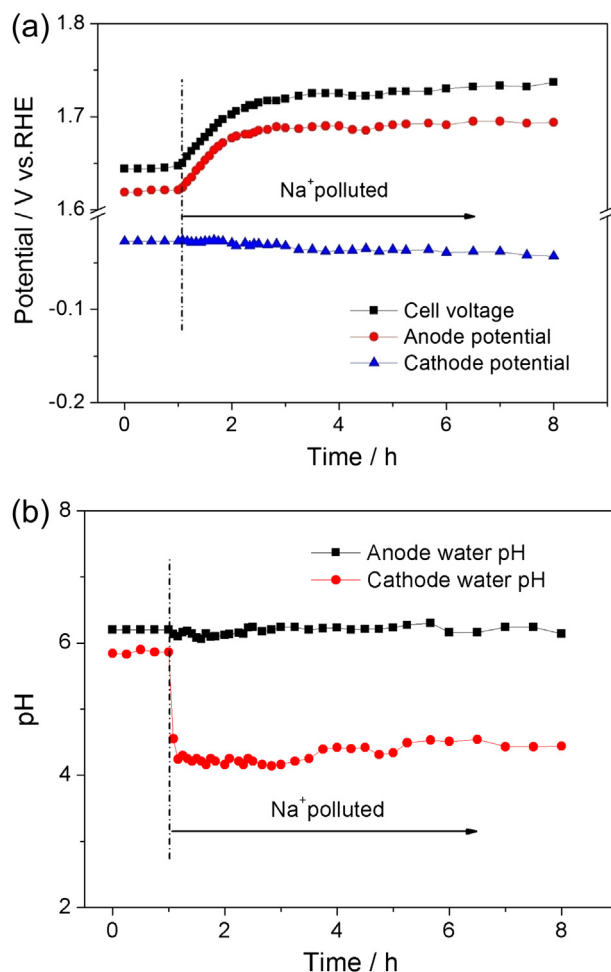


Fig. 9. (a) The effect of $0.001\text{ mol L}^{-1}\text{ Na}^+$ on the cell performance by cathode poisoning. (b) Anode and cathode water pH vs. time.

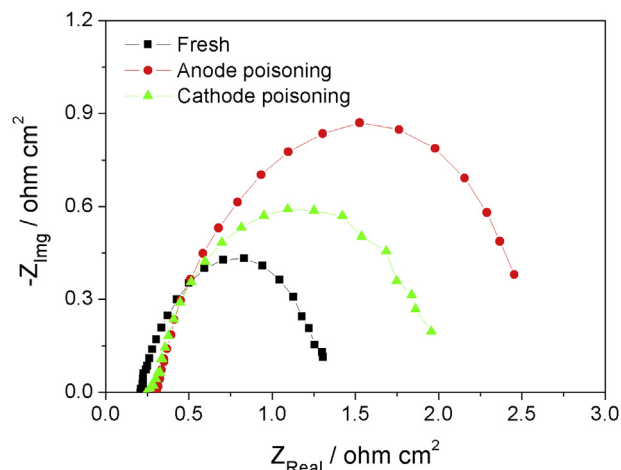


Fig. 10. Comparison of Nyquist plots for the fresh, anode-poisoned and cathode-poisoned SPE cells.

However, the cathode potential only decreased to -0.04 V in about 7 h. The voltage increase is mainly attributed to the increase of anode overpotential. The voltage increase caused by cathode poisoning is 0.09 V , while it is 0.63 V by anode poisoning. It is clear that the anode poisoning has severer effect on the cell performance than that of the cathode poisoning.

Fig. 9(b) shows the changes of the anode and cathode outlet water pH values during the cathode poisoning. Similar to the cathode poisoning at high Na^+ concentration (0.05 mol L^{-1}) [20], the anode outlet water pH was stable during poisoning, and the cathode outlet pH decreased from 5.6 to 4.2 immediately and became stable from then on. The distribution of sodium ions is governed by both the electric field and concentration gradient. Sodium ions are driven from the cathode to anode by concentration gradient, whereas from anode to cathode by electric field. As a result, the distribution of sodium ion finally gets equilibrium in the MEA and cathode feed water [28]. The protons exchanged with sodium ions enter into the cathode water. Consequently, there are enough protons for cathode reaction and the reaction (1) does not take place at the cathode for the cathode poisoning.

The typical Nyquist plots of electrochemical impedance in Fig. 10 are recorded at 1.45 V which corresponds to the oxygen evolution region. The impedance parameters are obtained by fitting the experimental data using ZSimpWin software and listed in Table 2. According to Table 2, the R_{Ω} and R_{ct} of cathode poisoning are $0.25\text{ }\Omega\text{ cm}^2$ and $1.80\text{ }\Omega\text{ cm}^2$, respectively, which are smaller than that of anode poisoning ($0.31\text{ }\Omega\text{ cm}^2$ and $2.40\text{ }\Omega\text{ cm}^2$). This indicated that there are less amount of Na^+ entering into the MEA by cathode poisoning than that of anode poisoning for the reverse migration direction of Na^+ driven by electric field and concentration gradient. The changes of R_{Ω} imply that the ohmic overpotentials, 50 mV and 20 mV at 500 mA cm^{-2} after anode and cathode poisoning, are not the primary reason for cell voltage increase. Moreover, the changes of R_{ct} are striking, which imply that the performance deterioration primarily comes from the kinetics loss for the lack of available protons replaced by Na^+ in the TPB of the catalyst layers [13,19].

Table 2

Ohm resistance of the cell polluted by anode poisoning and cathode poisoning with $0.001\text{ mol L}^{-1}\text{ Na}^+$.

Sample	Fresh	Anode poisoning	Cathode poisoning
$R_{\Omega}\text{ (}\Omega\text{ cm}^2\text{)}$	0.21	0.31	0.25
$R_{\text{ct}}\text{ (}\Omega\text{ cm}^2\text{)}$	1.12	2.40	1.80

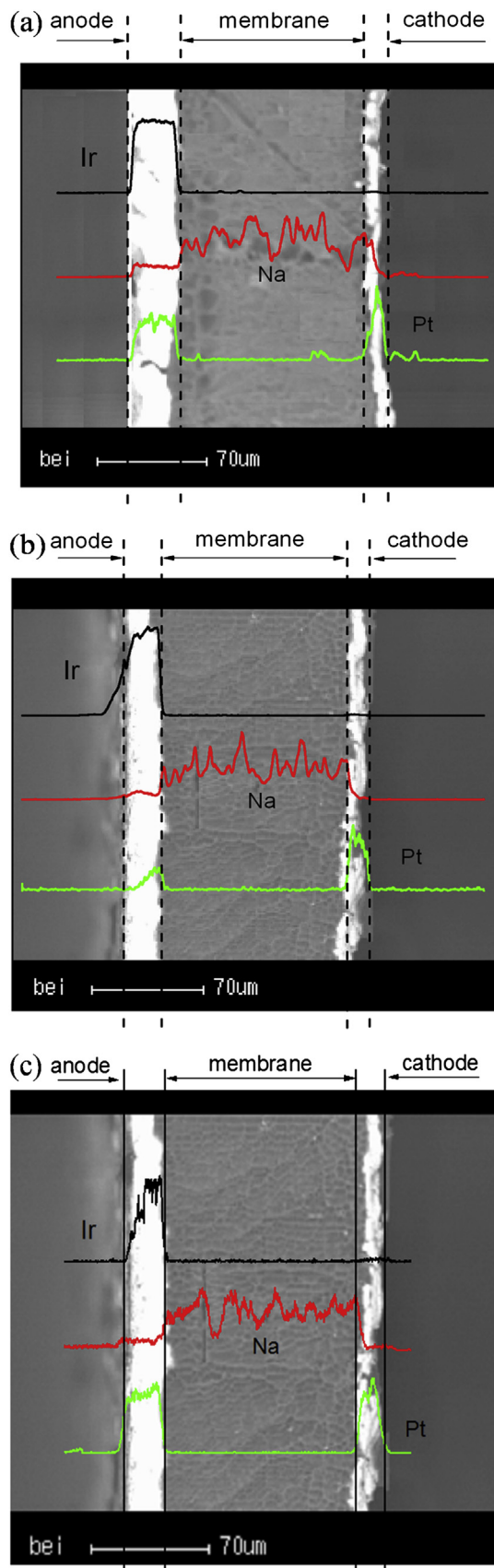


Fig. 11. EPMA images of the CCMs. (a) CCM polluted by anode poisoning; (b) CCM recovered with deionized water; (c) CCM polluted by cathode poisoning.

3.3. EPMA of CCMs

Fig. 11 shows the EPMA results of the cross-section of the CCMs. The distribution of Ir, Pt and Na can be clearly observed. Obviously, Na concentrates in the Nafion membrane in all CCMs for the low content of Nafion polymer electrolyte in the catalyst layers and higher affinity of Na^+ than protons for the sulfonic acid group sites [11–14]. In the CCM polluted by anode poisoning (Fig. 11a), a lower Na element content is detected in the anode catalyst layer than cathode catalyst layer, which proves that Na^+ migrates from the anode to the cathode and more concentrated on the cathode side than anode side. These results are consistent with the simulation reported by Kienitz et al. [19]. As shown in Fig. 11b, although the intensity of Na element in the anode and cathode catalyst layers is weaker than that in the membrane, Na still can be detected. Compare to Fig. 11a, Na element in the catalyst layers shows lower relative intensity than that in the membrane in Fig. 11b, which indicates that the concentration of Na decreases in the catalyst layers of CCM after being recovered with deionized water. The residual sodium ions increase R_{Ω} and R_{ct} (see in Fig. 4 and Table 1) and result in cell performance degradation (see in Fig. 2b). After cathode poisoning, the sodium ions can be detected in the anode catalyst layer (Fig. 11c). It indicates that the sodium ions are driven from cathode to anode by concentration gradient, which will increase ohmic resistance and anode overpotential.

4. Conclusions

The dynamic-state effect of low concentration of Na^+ on the SPE water electrolysis cell performance under different cell operating conditions was studied. The cell performance is degraded severely in the presence of Na^+ impurity, and the degradation extent is severer for anode poisoning than that of cathode poisoning. The extent of performance deterioration depends on the concentration of Na^+ contaminant, feed water flow rate and cell temperature. With higher concentration of Na^+ impurity, faster flow rate and lower cell temperature, a higher poisoning rate and voltage increase are observed. The extent of voltage increase is sensitive to the concentration of Na^+ (even several ppm), but is not affected by the current density when the concentration of Na^+ in feed water is fixed. This is because the equilibrium concentrations of Na^+ are identical in the MEAs poisoned by the same concentration of Na^+ , which determines the extent of the cell voltage increase. The dramatic increase in the cell voltage was primarily attributed to the kinetics loss rather than the ohmic loss. A lack of available protons in the TPB of catalyst layers, which was caused by the replacement of H^+ by Na^+ , may lead to the increase in charge transfer resistance R_{ct} . At constant current density, the lack of protons at cathode causes the reaction $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ to take place by anode poisoning. However, this reaction does not take place by cathode poisoning because there are enough protons for cathode reaction. The cell performance can only be partially recovered by deionized water treatment for the residual Na^+ in the catalyst layers and membrane.

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